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**Pseudotenfold symmetry in pentane-solvated  $C_{60}$  and  $C_{70}$** 

R. M. Fleming, A. R. Kortan, B. Hessen, T. Siegrist, F. A. Thiel, P. Marsh, R. C. Haddon, R. Tycko, G. Dabbagh, M. L. Kaplan, and A. M. Mujsce

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Crystals of  $C_{60}$  or  $C_{70}$  cocrystallized with *n*-pentane grow as elongated, ten-sided columns. X-ray diffraction shows ordering of  $C_{60}$  or  $C_{70}$  molecules along the column and a remarkable tenfold symmetry normal to the column. The ratio of the x-ray-diffraction vectors of the two lowest-order diffraction spots is nearly equal to the "golden ratio,"  $\tau$ . Despite these similarities with decagonal, quasicrystalline order, the diffraction indicates crystalline order with a twinned unit cell.

The production of bulk quantities of the fullerenes,  $C_{60}$  and  $C_{70}$ , has stimulated considerable interest in the synthesis and properties of these forms of carbon.<sup>1,2</sup> The fact that  $C_{60}$  molecules are truncated icosahedra has provided additional excitement by promoting speculation that unusual structures would result from the packing of  $C_{60}$ . Normally one does not expect the point symmetry of molecules to play a major role in determining the space group of the corresponding molecular compound. However, given the large size of the  $C_{60}$  molecule and the fact the crystal contains only  $C_{60}$ , it was initially surprising that  $C_{60}$  crystals grown by sublimation formed on a face-centered, close-packed cubic (fcc) lattice<sup>3</sup> rather than one of the structures known to result from the packing of icosahedra, e.g., body-centered cubic (bcc).<sup>4</sup>

An explanation of the nonicosahedral character of the cubic  $C_{60}$  structure is apparently a result of dynamic rotations of  $C_{60}$  molecules in the crystal. Solid-state NMR experiments indicate that the  $C_{60}$  molecule is freely rotating in the solid at room temperature and does not freeze-out until reaching temperatures of 50–100 K.<sup>5</sup> Since the x-ray results<sup>3</sup> indicate long-range translational order of spheres but inconsistent intensities in a structural refinement, the picture that emerges is an fcc lattice of  $C_{60}$  molecules with ordered mean positions of spheres, but rotational disorder between spheres. The rotations average out the icosahedral point symmetry and the cubic lattice is selected by van der Waals forces and ordinary sphere packing.

In this paper we describe the unit cell and symmetry of a modified structure that occurs when either  $C_{60}$  or  $C_{70}$  is cocrystallized with *n*-pentane to form the molecular crystal of the type  $C_{60} \cdot n\text{-C}_5\text{H}_{12}$ . The needle-shaped crystals have a remarkable ten-sided morphology and tenfold diffraction reminiscent of quasicrystalline, decagonal materials,<sup>6,7</sup> but the diffraction is consistent with crystalline order and twinning. The structure has a monoclinic primitive cell with  $\beta^* = 72.3^\circ$  that can also be described as an *A*-centered orthorhombic cell.

We prepared  $C_{60}$  and  $C_{70}$  powders using the process described by Krätschmer *et al.*,<sup>2</sup> and separated the two species by alumina column chromatography.  $C_{60}$  crystallizes into a cubic close-packed (fcc) lattice when powder is produced by solvent evaporation or when the material is sublimed<sup>3</sup> at temperatures above 300–500°C. In con-

trast, we find that most crystals grown from solutions with aromatic solvents are needle shaped with a large amount of rotational disorder about the axis of the needle. (A few crystals, particularly those with flat habits, have the fcc structure.) We have discovered that the disorder in the needle-shaped crystals is dramatically reduced by the addition of pentane vapor to the solution. We used a closed, *H*-shaped vessel to slowly diffuse pentane vapor from one arm into a solution of  $C_{60}$  or  $C_{70}$  located in the other arm. The rate of crystallization can be controlled by the relative temperature of the two arms of the cell. Usually, both arms of the cell were kept near or slightly below room temperature and crystallization occurred in about 12 h.

Crystals were characterized by x-ray diffraction from a rotating anode source with Cu  $K\alpha$  radiation. Preliminary orientation, symmetry, and unit-cell determinations were made using precession photographs taken using a Ni filter. Single-crystal scans were made on a four-circle diffractometer using a focusing pyrolytic graphite monochromator and a flat analyzer. Additional resolution was provided by 1-mm slits before and after the analyzer. X-ray scattering from crystals grown from benzene solutions gave similar results with similar unit cells for both  $C_{60}$  and  $C_{70}$ . Only the magnitude of the lattice parameters is different in the two materials.

X-ray precession photographs of crystals obtained by pentane-benzene interdiffusion show that the crystals are ordered along the needle axis with a *d* spacing of 10.1 Å for  $C_{60}$  and 10.5 Å for  $C_{70}$ . This is the same ordering earlier observed for the disordered crystals grown by evaporation from pure benzene solutions. The diffraction symmetry normal to the needle, shown in Fig. 1, indicates that the crystals are twinned in a highly unusual way. The most striking feature is the near perfect tenfold-symmetry that is apparent in the plane normal to the needle axis. The tenfold-symmetry can also be seen in the crystal morphology as shown in Fig. 2 where we show a scanning-electron-microscope (SEM) image of a  $C_{60}$  crystal. (The wavy features in the SEM photograph are artifacts resulting from charging of the sample.) Tenfold symmetry on one plane and ordering normal to the plane are characteristics of decagonal quasicrystalline order.<sup>6,7</sup> An additional intriguing feature of Fig. 1 is the ratio of x-ray-momentum transfers of the two lowest-order-dif-

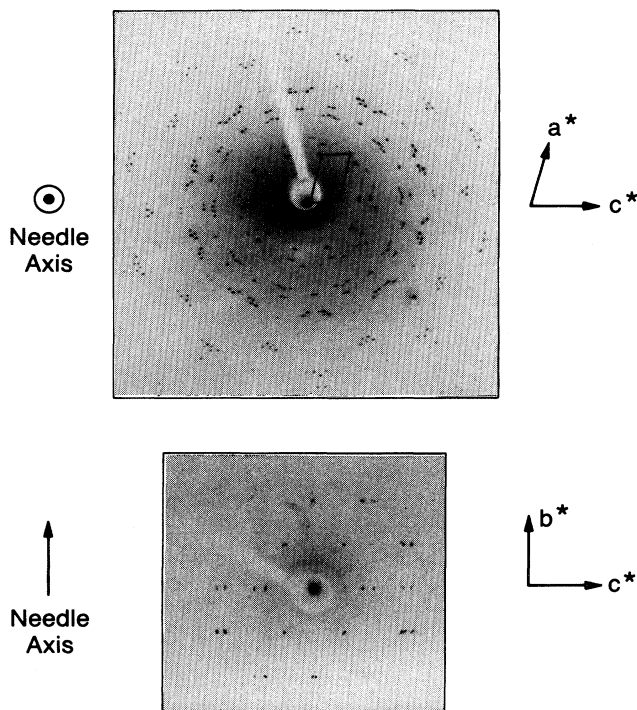


FIG. 1. Precession photographs from a crystal of  $C_{60} \cdot n\text{-}C_5H_{12}$ .

fraction spots along any one of the tenfold radii. The ratio is 1.627 for  $C_{60}$  and 1.632 for  $C_{70}$ , numbers close to the "golden ratio,"  $\tau = [(5)^{1/2} + 1]/2 = 1.6180$ . Scattering vectors with a ratio equal to  $\tau$  are another of the characteristics of quasicrystalline diffraction.<sup>8</sup> (The diffraction symmetry of  $C_{70}$  crystals grown by the same method is identical with that shown in Fig. 1, but with larger lattice parameters.)

Despite the superficial similarities with quasicrystalline diffraction, it is straightforward to show that the diffraction is consistent with crystalline diffraction from a twinned unit cell. A crystalline monoclinic cell with  $\beta^* \approx 72^\circ$  can be constructed by identifying one of the

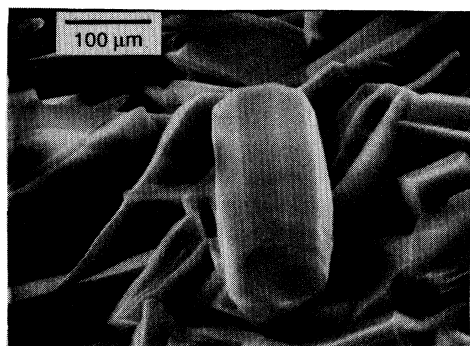


FIG. 2. SEM photograph of crystals of  $C_{60}$  grown from solutions with benzene. This photograph has distortions due to sample charging and movement.

inner ring of spots as  $c^*$  and one of the next ring of spots as  $a^*$  as shown in the unit-cell outlined in Fig. 1. Twins formed by rotations of this primitive cell about  $b^*$  can account for all diffraction spots. Twinning of any close-packed structure is ruled out by the observation of the lowest-order monoclinic spot, the (001), which corresponds to a  $d$  spacing of 15.8 Å for  $C_{60}$  and 16.4 Å for  $C_{70}$ . The 16-Å-diffraction spot is not allowed in any close packing of 10-Å spheres. We measured the lattice parameters by placing the twinned crystals on a four-circle diffractometer, orienting using one twin and measuring the  $d$  spacings of about ten reflections. These observations were input to a least-squares program normally used to refine unit cells from powder-diffraction data. For  $C_{60}$ , the lattice parameters are  $a = 10.14(3)$ ,  $b = 10.08(3)$ ,  $c = 16.5(5)$ , and  $\beta = 107.73^\circ(3)$ . For  $C_{70}$ , we obtained  $a = 10.618(6)$ ,  $b = 10.529(6)$ ,  $c = 17.33(1)$ , and  $\beta = 107.70^\circ(3)$ . (Further cell reduction results in an  $A$ -centered orthorhombic unit cell, but to make the twinning operations and the relationships to the fcc cell clear, we will continue to express the cell dimensions in terms of the primitive monoclinic cell.)

A sphere-packing model that is consistent with the unit cell and the twinning is shown in Fig. 3(a). The model can be visualized as stacked, square-planar planes of spheres. If the top plane were close packed, the result would be a body-centered-tetragonal cell that is equivalent to an fcc-cell rotated by  $45^\circ$ . Instead, this layer is displaced in the model by half a lattice constant along a cubic [110] direction. The result is a primitive monoclinic cell with channels, as in a clathrate, running parallel to the monoclinic  $b$  axis (formerly a cubic [110] direction). For spheres of diameter  $D$ , the model predicts lattice parameters of  $a = b = D$ ,  $c = 1.651D$ , and  $\beta = 107.63^\circ$ . The model has the characteristic 16-Å-diffraction line and lattice parameters that are remarkably close to the observed

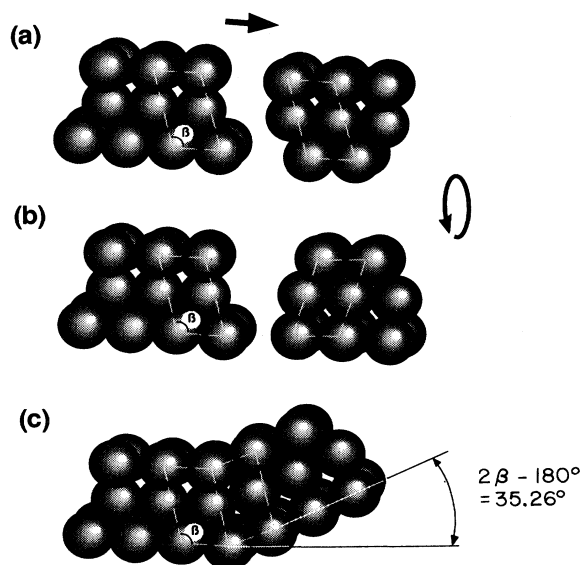


FIG. 3. Proposed packing of spheres showing how twinning can induce rotations of the unit cell about the  $b$  axis.

values.

Figure 3 summarizes the formation of twins and the resulting pseudotenfold-symmetry crystal morphology. Conceptually, one can view the formation of a twin by first rotating the unit cell  $180^\circ$  about the  $a$  axis as in Fig. 3(b) and then by  $2\beta - 180^\circ = 35.26^\circ$  about the  $b$  axis as in Fig. 3(c). If we form successive domains of this type, the result is pie-shaped domains that form the shape depicted in Fig. 4. Notice that the twinned model has an almost regular ten-sided morphology. For the hard spheres, the gap in the solid is  $360^\circ - 352.6^\circ = 7.35^\circ$ .

A gap of nearly the same magnitude can be observed in the twinned crystals. Azimuthal scans through each of the (100) and the (001) twins of a  $C_{60}$  crystal are shown in Fig. 5. For this crystal, nearly all of the scattering comes from three domains as indicated by the solid-tie lines. Each (100)-(001) pair is separated by  $72.3^\circ$ , the monoclinic  $\beta^*$  angle. The No. 1 domain in Fig. 5 has an additional peak corresponding to a twin rotated in the opposite sense, as is indicated by the dashed-tie line. Adjacent pairs of (001) peaks or (001) peaks are separated by  $35.5^\circ$ , the twinning angle. Since the twinning angle is slightly less than  $36^\circ$ , a crystal that is completely twinned would have a gap of  $5.0^\circ$ . In the ordered crystals obtained by growth from pentane-benzene interdiffusion, there is an alignment of the gap from one layer to the next, and one sees a finite number of twinned reflections. In the disordered crystals rapidly grown from pure benzene solutions, the gap is not aligned and one observes a smearing of the diffraction spots azimuthally.

The channels in the model have a diameter of about  $3.6 \text{ \AA}$  that apparently contain solvent molecules. We measured the solvent content of one batch of crystals by dissolving a weighed quantity of material in  $CS_2$ . Proton NMR indicated an overall crystal stoichiometry of  $C_{60} \cdot n\text{-}C_5H_{12}$  with trace benzene at the level of 5 mol%. Since the model contains two fullerene molecules per channel, this implies an occupancy of two pentane molecules per unit cell for this batch of crystals. We are not certain if this stoichiometry is fixed, or if this structure

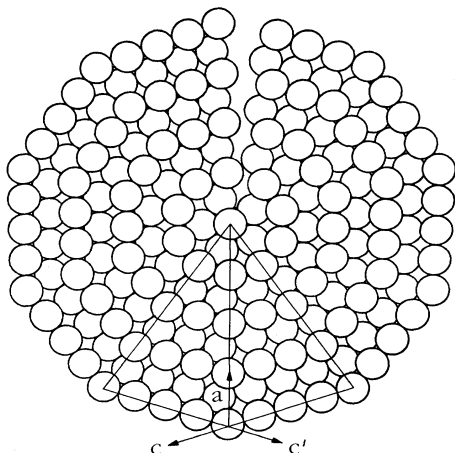


FIG. 4. A fan-shaped collections of twins showing how a ten-sided object with a  $7.35^\circ$  gap can be constructed.

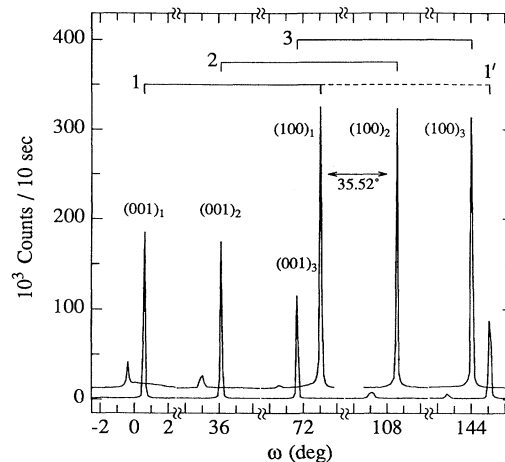


FIG. 5. Azimuthal  $\Omega$  scans through five of the twinned (100) and (001) peaks of the monoclinic cell. These peaks correspond to the first and second rings of the spots in Fig. 1.

can be obtained using other solvents. For example, the crystal shown in Fig. 2 was obtained by evaporating benzene with no addition of pentane vapor. The role of the pentane may be to align the channels rather than to stabilize the phase itself.

The hard-sphere packing described here reproduces the observed lattice parameters and twinning extraordinarily well. This would suggest, that like fcc  $C_{60}$ , the internal symmetry of the molecule does not influence the overall symmetry of the structure. Pseudofivefold symmetry has been observed in the nonequilibrium, twinned growth of other materials, e.g., dendritic copper<sup>9</sup> and silver films.<sup>10</sup> It is, therefore, likely that the tenfold twinning reflects a nucleation process of the type observed in small clusters of atoms<sup>11</sup> rather than a reflection of internal icosahedral symmetry.

The question of whether or not the internal symmetry of  $C_{60}$  is important in determining the structure has implications on the intriguing possibility that quasicrystalline or decagonal  $C_{60}$  could be made under the proper conditions. A description of the microscopic building blocks of quasicrystals remains an active area of research with several key questions still unresolved. The limits of the discussion include tiling of objects with different shapes<sup>12</sup> and glasslike packing of icosahedral shapes.<sup>13,14</sup> Under both approaches, one would expect that nearby crystalline phases would exhibit features or subunits containing icosahedral symmetry, as is seen experimentally.<sup>4,15</sup> Under both approaches one would expect the possibility of quasicrystallinity to be enhanced by cocrystallizing molecules with different shapes as is the case here.

In summary, we have observed pseudotenfold diffraction symmetry and morphology in twinned crystals of the type  $C_{60} \cdot n\text{-}C_5H_{12}$ . We propose a structure that can be derived from the fcc cubic structure by displacing molecules by half a lattice constant along the cubic [110] direction. This produces channels in the close-packed structure that, according to proton NMR measurements, contain one pentane molecule per  $C_{60}$  or  $C_{70}$ , however we

note that it may be possible to stabilize the phase without using pentane. The model structure can be twinned to produce domains rotated by  $35.3^\circ$ , in close agreement with measurements of domain rotation. We suggest that the tenfold twinning does not result from the internal symmetry of  $C_{60}$ , but point out that if materials with

icosahedral subunits could be made, one might have the building blocks for making a quasicrystalline form of  $C_{60}$ .

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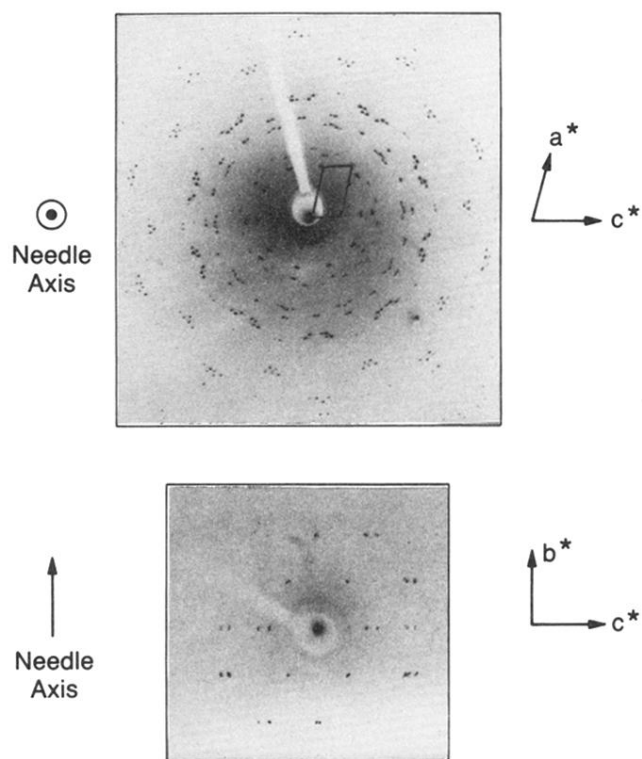


FIG. 1. Precession photographs from a crystal of  $C_{60} \cdot n-C_5H_{12}$ .

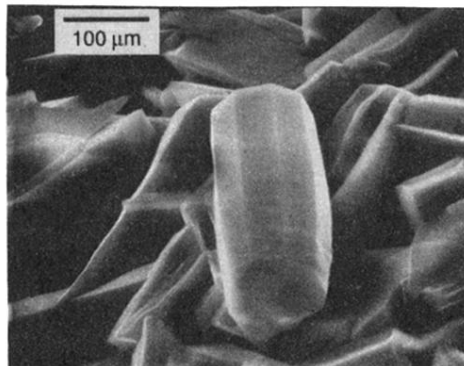


FIG. 2. SEM photograph of crystals of C<sub>60</sub> grown from solutions with benzene. This photograph has distortions due to sample charging and movement.

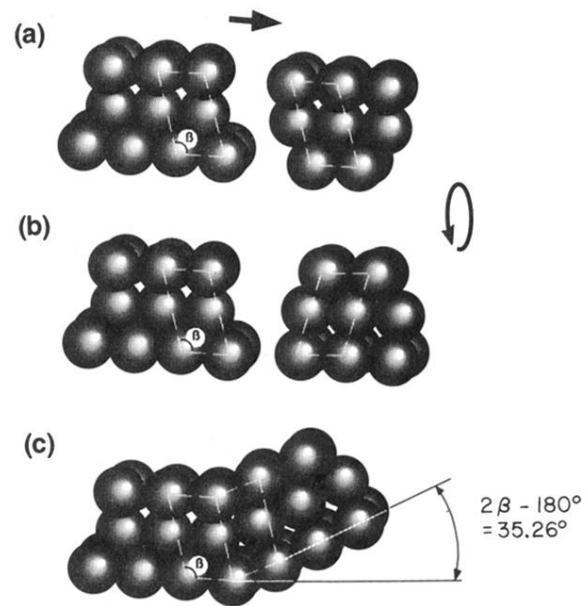


FIG. 3. Proposed packing of spheres showing how twinning can induce rotations of the unit cell about the  $b$  axis.